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Lead generation and separation mechanisms from lead silicate glass by reduction-melting

Hiroyuki INANO^{1,†}, Keiichi TOMITA¹, Tatsumi TADA¹ and Naoki HIROYOSHI²¹Industrial Research Institute, Hokkaido Research Organization, Kita 19 Nishi 11, Kita-ku, Sapporo 060-0819, Japan²Graduate School of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan

Reduction-melting is a method to separate lead from waste cathode ray tube (CRT) lead glass. To study the mechanism of lead separation, melting tests using model lead silicate glass rather than actual CRT glass were carried out. Crushed model lead glass mixed with activated carbon (reducing agent) and Na_2CO_3 (flux) was heated and quenched at target temperatures to stop the reaction. Tomographic images of the quenched samples were observed by X-ray computed tomography. Further, the samples were evaluated by X-ray diffractometer, X-ray fluorescence spectrometer, and mass change determinations. From these results, it was found that reduction of lead glass and separation of lead occur with the following mechanisms. Elemental Pb (lead) was generated from below 973 K before the sample had melted completely. At 1273 K and above, whole of the sample had become a melt, and the Pb separated and settled out of the glass. Gas released during the melting process agitate the melt and promote the Pb settling.

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1. Introduction

Recently TV sets have changed from massive Cathode ray tube (CRT) to flatter and lighter Liquid Crystal Displays (LCD), and the production of CRT TV tubes have decreased steeply. As a result, it has become impossible to recycle CRT glass cullet in new CRT tubes by the so far commonly employed “closed loop recycling”. Discarding of CRT TV tubes continues at present, and the disposal of used CRT components has become an issue. A CRT is composed of three different glass parts, each with different chemical compositions,^{1,2)} and cannot be used as raw material for other mass-produced glass, such as sheet glass and bottles. Especially the rear funnel part contains up to 25 mass % of harmful PbO which is difficult to utilize. Because lead is a high-demand base metal for industrial use such as battery electrodes in automobiles, recovery of Pb from CRT glass would be very economically attractive. Commonly, Pb recovery methods are investigated by “dry processes²⁾⁻¹¹⁾” that treat materials at high temperatures and “wet processes^{12),13)}” that treat materials near room temperatures. The reduction-melting is a dry process and requires high temperatures of over 1300 K, and it has the advantage that Pb can be recovered as metal. When lead glass is mixed with reducing agent and heated at high temperature, the PbO in the glass is reduced to Pb. In this

process, the glass viscosity increases with the decreases in the PbO concentration in the glass, and the generated Pb particles remain suspended in the glass.⁷⁾ When adding a flux like Na_2CO_3 to the glass to decrease the viscosity, the high specific gravity Pb is settled and the separated Pb can be recovered from the glass.²⁾⁻⁶⁾

Knowledge of Pb generation in lead glass and the Pb separation mechanism from glass is useful to optimize the reduction-melting process. There are many details of this that are not known and need to be clarified because research into the details of the mechanisms are lacking. In past studies, the distribution of lead in the glass after melting was studied optically by observation of cut cross-sections. This method results in the disadvantage that the state of the lead distribution depends on the position of the cut of the samples. In the research fields of biomedical¹⁴⁾ and material engineering,¹⁵⁾⁻¹⁸⁾ X-ray computed tomography (X-ray CT) is a common nondestructive observation technique. In glass research X-ray CT has been applied to observe the melting conditions at high temperature,¹⁹⁾ forming processes,²⁰⁾ and self-healing of cracks.²¹⁾

In this study, X-ray CT was used as the technique to observe the 3D-distribution of lead and bubbles in the reduction of the melted glass. Specifically, crushed lead glass, reducing agent, and flux were mixed and placed in a crucible and then heated. When this mixture reached the target temperature, samples were quenched to stop the reaction, and then the state of the sample was observed by X-ray CT. Combining the X-ray CT results with the results

[†] Corresponding author: H. Inano; E-mail: inano-hiroyuki@hro.or.jp

of X-ray diffractometer (XRD) and X-ray fluorescence spectrometer (XRF) analyses and mass changes during the reaction, the settling and separation mechanisms of lead in the process of lead glass reduction-melting is discussed.

2. Experimental

2.1 Materials

Actual CRT funnel glass is composed more than 10 kinds of oxides, and it has a complicated chemical composition. In this study, model glass that simulated actual CRT funnel glass but contained only four kinds of specified oxides was used. The chemical compositions of the oxides that make up in more than 1 mass % in actual CRT funnel glass and the model glass are shown in **Table 1**. The ratios of SiO₂, PbO, and Al₂O₃ are very similar to the actual CRT funnel glass, and the several kinds of alkali and alkali earth metal oxides in the actual CRT glass are represented by one oxide Na₂O. The model glass was crushed and it was used in grain sizes smaller than 1 mm. The tests used Na₂CO₃ (Sigma-Aldrich Japan) as a flux (viscosity reducing agent for melted glass), and activated carbon powder (trade name: charcoal, activated, powder, Wako pure chemical industries Ltd.) with grain sizes of a few μm to 20 μm as the reducing agent.

2.2 Melting tests

Volumes of 20.0 g of model glass, 10.6 g of Na₂CO₃, and 1.2 g of activated carbon (C) were mixed with alumina mortar and placed in a 30 ml alumina (99.5%) crucible and covered with an alumina (99.5%) cover. From 2 to 4 such crucibles were set in an electric furnace at room temperature without adjusting the surrounding air, and heated at a heating rate of 300 K/h. When the furnace temperature reached the target temperature between 673 to 1373 K, crucibles were removed from the electric furnace and left to cool outside. This process was used to quench the samples and the chemical reactions at the heated temperature stopped. The samples in the crucibles were weighed before and after the heating, also, the mass change of an alumina crucible without sample heated to 1473 K was determined as less than 0.01 g.

2.3 Characterization

The samples in the crucibles cooled to room temperature were observed by a microfocus X-ray CT system (inspeXio

SMX-225CT, Shimadzu Co., Japan). Here, a crucible was irradiated by X-rays from cross directions and rotated through 360 degrees at room temperature for the tomographic data. The X-ray CT scanning was performed at an accelerating voltage of 200 kV and a current of 40 μA, with a 0.5 mm Cu plate filter, and a voxel size was 0.1 mm. The 3-D image processing was performed using VGStudio Max software (Volume Graphics GmbH, Germany).

After the X-ray CT scanning, samples were observed visually and by a digital microscope (KH-1300, Hirox, Japan). The samples heated to 1173 K or less were in the powder state and were not melted completely, and samples of the powder taken from the crucibles were observed. The samples heated to 1223 K and above were melted and here cross-sections of the samples were observed. Samples heated to 1273 and 1323 K were cut by a diamond wheel saw with water cooling and the cross sections were observed. Here, unreacted chemical agent remained in the sample heated to 1223 K and it was confirmed that the remaining agent would react with water. To accommodate this, a fracture surface for observation was created by breaking the sample in the crucible with a hammer. The sample heated to 1373 K was sliced by a diamond wheel saw and its surface was polished, then observed by an optical digital microscope with transmitted light.

After the residual glassy phase of the samples was ground and visible Pb particles were removed, crystalline phase identification and chemical composition analysis were carried out. The crystalline phase identification was carried out by an XRD (Ultima IV, Rigaku Co., Japan) with CuKα radiation, and data were collected with an accelerating voltage of 40 kV, current of 30 mA, angular range of 10 to 70 degrees, scanning steps of 0.01 degrees, and scanning speed of 2 degrees/min. The chemical composition analysis was carried out by an XRF (ZSX Primus II, Rigaku Co., Japan), using the fundamental parameter method for elements with atomic numbers from 11 (Na) and the chemical composition converted to oxide mass % was calculated.

3. Results and discussion

3.1 X-ray CT and cross-sectional visual observations

The X-ray CT 2D images of the starting material and samples heated to 973–1373 K are shown in **Fig. 1**; samples heated to temperatures below 973 K were also observed by X-ray CT but are not shown as they did not show obvious differences from the sample heated to 973 K.

Overall, the 2D images of the 973 and 1073 K samples do not differ from the starting material. Visual observation showed that the greater part of the samples did not sinter and melt, and that they were a mixture of the starting material powders. These results confirm that most of the model glass, Na₂CO₃, and activated carbon in the starting material remained unreacted at these temperatures.

In the images of the samples heated to 1173–1323 K, there are black areas at the upper part of the sample heated to 1173 and 1223 K, at the sides of the 1273 K samples, and

Table 1. Chemical compositions of actual CRT funnel glass, and the model glass used in this study

Oxide	Actual CRT Funnel glass		Model glass	
	mass %	mol %	mass %	mol %
SiO ₂	49.4	63.9	53.8	67.9
Al ₂ O ₃	3.5	2.7	4.2	3.1
PbO	22.2	7.7	25.1	8.5
Na ₂ O	6.3	7.5	16.7	20.4
K ₂ O	8.4	6.9		
MgO	1.6	3.2		
CaO	3.8	5.3		
SrO	1.5	1.2		
BaO	1.8	0.9

Fig. 1. X-ray CT images of the starting material and heated samples. White areas are Pb.

Fig. 2. Cross-sectional photo of the sample heated to 1223 K.

Fig. 3. Microscope image of the sample heated to 1273 K.

throughout the whole area of the 1323 K sample cross section. These black areas show bubbles that have low density and low X-ray absorption coefficients and are speculated to be CO_2 generated by the reaction of Na_2CO_3 and glass, or CO generated by the reaction of activated carbon and CO_2 , as will be described further below. When the fracture surface of the sample heated to 1223 K was observed visually (Fig. 2), it was found that, at the upper and side parts appeared gray and that grains become larger by the melting reaction of model glass with Na_2CO_3 . At the center and the bottom of the sample it appeared black due to remaining activated carbon. It is assumed that no reaction of the model glass with Na_2CO_3 had taken place in this area, as both the reaction of glass with Na_2CO_3 and the reaction of the generated CO_2 with C are endothermic reactions, and the heat introduced into the crucible did not penetrate to here, leaving the temperature of the center of the sample lower than the surroundings. Based on this, the reaction at 1273 K can be seen to have proceeded throughout the whole of the volume in the crucible, as 1 to 5 mm diameter bubbles are distributed throughout the whole area in the sample in the crucible (Fig. 1). According to the cross-sectional observations of the sample heated to this temperature (1273 K,

Fig. 3), the sample was agglomerate of approximately 1 mm granules and had continuous pores.

The 2D images of samples heated to 1323 and 1373 K in Fig. 1 indicate that samples shrank overall, more than those heated to lower temperatures, suggesting that pores are disappeared by the reaction. There are many bubbles throughout the sample heated to 1323 K, but few bubbles in the sample heated to 1373 K. Also, the presence of a large Pb particle (white area with large X-ray absorbance coefficient) is visible in the 1373 K sample. Figure 4 shows 3D X-ray CT images of Pb in samples heated to 1323 and 1373 K. These images suggest that small lumps of Pb are dispersed throughout the sample heated to 1323 K; in the 1373 K sample there is one large lump of Pb resting at the bottom of the crucible. This indicates that Pb generated by reduction has condensed and settled as a lump of Pb in the 1323–1373 K temperature range.

The glassy part of the sample heated to 1373 K was sliced and these thin samples were observed in an optical digital microscope with transmitted light. The result (Fig. 5) shows dispersed black particles of less than 1 μm . As will be described below, Pb was determined by XRD in this sample and it may be concluded that these black

Fig. 4. Three-D X-ray CT images of Pb in samples heated to 1323 and 1373 K.

Fig. 5. Transmitted light microscopic image of a slice of sample heated to 1373 K.

Fig. 6. XRD patterns of samples heated to 923–1373 K.

particles would be Pb particles. This result confirms that a part of the Pb remains in the glass melt without condensing and settling in the 1373 K sample.

3.2 XRD

The XRD patterns of the glassy phase in the samples heated to 923–1373 K are shown in Fig. 6. The enlarged XRD patterns of the samples heated to 923 and 973 K are shown in Fig. 7. All of the Na_2CO_3 , Pb, and sodium metasilicate (Na_2SiO_3) peaks can be identified in the XRD patterns.

Fig. 7. Enlarged XRD patterns of samples heated to 923 and 973 K.

Fig. 8. Plot of PbO concentrations in samples versus heating temperature. The value for the starting material (298 K) is for a mixture of model glass and Na_2CO_3 , without activated carbon.

Below 1223 K, Na_2CO_3 was present and these peaks disappeared at higher temperatures, presumably because Na_2CO_3 had reacted with the model glass. The peak patterns of Na_2SiO_3 that were generated by the reaction between the model glass and the Na_2CO_3 in the samples heated to 1173–1323 K were not present at 1373 K, a temperature above the melting point of Na_2SiO_3 (1361 K). Pb was identified above 973 K but not at lower temperatures (Fig. 7). The peak intensity of Pb increased with increasing temperature until 1273 K and became weaker in samples heated to temperatures above 1323 K. It is assumed that the XRD peak intensity weakened due to a decreasing concentration of Pb in the glass melt brought about by the condensation and settling of Pb as detailed in section 3.1.

3.3 Chemical analysis by XRF

Figure 8 shows the relationship between the amount of Pb in the glassy phase (PbO concentration analyzed by XRF, in oxide conversion value) and the temperatures the samples were heated to. The analysis showing all components in the sample heated to 1373 K is shown in Table 2.

Table 2. XRF results for the sample heated to 1373 K

Oxide	Na ₂ O	Al ₂ O ₃	SiO ₂	PbO
mass %	43.7	4.0	49.2	3.0
mol %	44.2	2.7	51.7	1.5

Fig. 9. Mass changes of heated samples.

From Fig. 8, the PbO concentration was about 20 mass % at temperatures below 1073 K and decreased steeply with increasing temperature, it was 3.0 mass % in the 1373 K sample, the maximum temperature in this study. In summary, these results suggest that Pb was generated by the reduction reaction, settled, and increasingly eliminated from the glassy melt at the final sample temperatures above 1073 K. From the X-ray CT observations detailed above (Fig. 1), lumps of Pb settled at the bottom of the crucibles with samples heated to above 1323 K only, and not with samples reaching temperatures below 1273 K. The reason why the Pb component value decreased between 1073 and 1323 K is that large Pb grains generated in the glassy phase were eliminated when samples were ground and sieved.

3.4 Mass changes

Model glass, Na₂CO₃ (flux or viscosity reducing agent), and activated carbon (reducing agent) solid were parts of the samples in the crucibles, and during the heating the mass of the solid sample decreased due to processes such as CO₂ generation by the reactions of the components taking place during the heating process. The relationship between the heating temperature and the mass change is shown in **Fig. 9**. Activated carbon (1.2% of the sample) burns at 700 to 810 K in air, but according to the experimental results, the sample mass decrease in the 873 K sample is only 0.6% (equivalent to 0.2 g). This value is small considering the activated carbon mass contained in the starting material, it suggests that only little of the activated carbon has burned. The crucibles were covered with a lid and only a little air was present in the crucibles during the heating, then from this it may be assumed that only a little of the activated carbon has burned due to the reaction

Table 3. Disappearing components during the reaction and its fraction

Starting materials		Disappearing fraction	
component	mass/g	component	mass/g
Model glass	20.0	O in PbO	0.4
Na ₂ CO ₃	10.6	CO ₂	4.4
Activated carbon	1.2	C	1.2
Total	31.8		6.0

with the little oxygen in the air available, leaving some activated carbon unreacted.

The mass of the samples decreased steeply at temperatures from the sample heated to 1023 K. The steep decrease in the mass continued until 1323 K, but there was a less steep mass decrease at the temperatures above this. In total, the rate of decrease from the starting material weight was 18.6%. Now, assuming that all of the O in the PbO, CO₂ in Na₂CO₃, and also the activated carbon gasifies and disappears from the sample, this mass decrease is calculated to be 18.9% from the sample composition in **Table 3**. The actual mass decrease (18.6%) shown in Fig. 9 agrees well with this calculated value.

3.5 Chemical reaction and glass viscosity

In the removal and recovery processes of the Pb by the reduction melting method, it is important to consider the condensing and settling phenomena of the Pb. The glass viscosity greatly affects these processes, and depends strongly on both the temperature of the sample and on the chemical composition of the components.

The model glass contains SiO₂ as a network-former oxide (NWF) that has strong covalent bond properties forming a 3D network structure. In addition, the original sample contains Na₂O and PbO as network modifier oxides (NWM) which break up the network, and Al₂O₃ as an intermediate oxide. Generally, glass viscosity increases with increasing NWF ratios in the glass, and decreases with increasing NWM ratios. When the model glass with added Na₂CO₃ and activated carbon is heated, there are a reaction of the glass with the Na₂CO₃, a reaction of CO₂ with the activated carbon, and reduction of PbO. As a result, the change in the relative ratios of SiO₂, Na₂O, and PbO affect viscosity greatly. The Na₂CO₃ added as a flux (viscosity reducing agent) reacts with the SiO₂ component in glass as below.

Where $\equiv$ in this equation indicates three Si–O bonds. Breaking up the 3D network of SiO₂ bonds that have strong covalent bond properties would increase the fluidity and decrease the viscosity of the melt.

The reaction of CO₂ generated due to the Na₂CO₃ with activated carbon (C) produces CO (Boudouard reaction).

The PbO in glass is reduced by C and CO.

Elimination of PbO as NWM from the glass by this reaction increases the melt viscosity.

As detailed above, the lead glass reduction melting process is a complex process with reactions causing both increase and decrease in viscosity, and it is particularly important to know the viscosity at the final stage of the process for a quantitative discussion of Pb settlement and separation. As shown in Table 2, the concentrations of SiO₂ and Na₂O in the glass are 51.7 and 44.2 mol % respectively, with the sum of the Al₂O₃ and PbO concentrations 4.2 mol %, then, disregarding Al₂O₃ and PbO gives an experimental viscosity value of $\log \eta$ (Pa·s) = 0.55 at 1373 K²²⁾ for a glass melt consisting of 55 mol % SiO₂ and 45 mol % Na₂O and this is used in the calculations below.

3.6 Settlement and separation of Pb from the glass melt

Separation of glass melt and Pb is achieved by the Pb settling from the glass melt. Based on the XRD results, the Pb generation has started at below 973 K, but at this temperature no Pb has settled from the sample. The Pb is denser than the glass melt, but even when the glass melt is very viscous at low temperatures, Pb does not settle. The presence of Pb precipitate was established at 1323 K and higher temperatures.

To evaluate the Pb settlement phenomena quantitatively, the relationship between the particle diameter, terminal velocity, and settling time was investigated by Stokes' law which provides a terminal velocity V_{Pb} (m/s) for particles in laminar flow.

$$V_{\text{Pb}} = \frac{gD_p^2(\rho_p - \rho_f)}{18\eta} \quad (5)$$

Here g is the acceleration of gravity ($= 9.8 \text{ m/s}^2$), D_p is the particle diameter (m), ρ_p is the Pb particle density (kg/m^3), ρ_f is the fluid (molten glass) density (kg/m^3), and η is the viscosity of the fluid ($\text{Pa}\cdot\text{s} = \text{kg/m}\cdot\text{s}$).

The density of Pb at 1373 K is estimated as 9660 kg/m^3 , calculated from the temperature dependence of Pb density reported in the literature.²³⁾ The density of a glass melt composed of 45 mol % Na₂O and 55 mol % of SiO₂ at 1373 K is estimated as 2250 kg/m^3 , obtained from literature data²⁴⁾ interpolation. The melt viscosity is estimated to be $10^{0.55} \text{ Pa}\cdot\text{s} = 3.55 \text{ kg/m}\cdot\text{s}$ from the considerations in the preceding section. These values were substituted into Eq. (5) and terminal velocity of the Pb was calculated. With this, the relationship between particle diameter, settlement velocity, and time to settle 20 mm in a glass melt are shown in Table 4. The total time of the reduction melting treatment from 298 to 1100 K is 3 h 36 min ($13 \times 10^3 \text{ s}$). From the Table 4 values, 0.1 mm or larger diameter Pb particles would be able to settle and separate from the glass melt. However, Pb particles of 0.01 mm or less would not be able to settle and separate from the glass melt, suggesting that they would remain suspended in the melt.

Table 4. Pb particle diameters and settling times in melt at 1373 K

Pb particle diameter /mm	Settling velocity /mm/s	Time to settle through 20 mm of glass/s
1	1.1	18
0.1	1.1×10^{-2}	18×10^2
0.01	1.1×10^{-4}	18×10^4

As shown in Fig. 5 however, the diameters of Pb particles remaining in the glass after heating to 1373 K were about 1 μm , much smaller than that estimated by the calculations (Table 4).

These results suggest that disregarding the effects of convection flows and agitation due to gas generation may have caused the disagreement of time to settle and particle diameter. For example, in bubble refining processes of glass production, the glass melt is agitated to promote collision and coalescence of bubbles. The resulting increase in bubble diameters accelerates the velocity of bubbles rising to the melt surface. Similarly, in the reduction melting process of lead silicate glass, the generated CO and CO₂ gases in Eqs. (1) to (4) agitates the melt, and this may be assumed to promote collisions and coalescence of the Pb particles and increase the diameters. It is thought that this effect resulted in settling velocity increases.

3.7 Total process

From the results reported above, the Pb separation from lead silicate glass by reduction melting is estimated to proceed through the processes that will be described below.

The starting material is a mixture of model glass (lead silicate glass), Na₂CO₃, and carbon [Fig. 10(a)]. During the heating, the Pb begins to be generated from the PbO in the glass by reduction at between 923 and 973 K. As the temperature rises further, the mass of the sample decreases by the release of CO₂ generated from the PbO reduction and reaction of the model glass and Na₂CO₃. Between 1073 to 1173 K crystals of Na₂SiO₃ begin to form, at 1273 K the sample in the crucibles is not completely melted while bonding of granular products with diameters of 1 mm create an open structure. Most of the generated gas (CO and CO₂) is released to the outside of the sample through the openings this creates [Fig. 10(b)].

At 1323 K, the whole sample is melted, and the openings in the structure of the melt have disappeared, resulting in the gas that is now generated becoming trapped in the melt. At temperatures above the melting point of Na₂SiO₃ (1361 K), the viscosity of the sample decreases steeply due to the melting of Na₂SiO₃ crystals. Then rapid evacuation of generated gas agitates the melt [Fig. 10(c)]. The gas now disappears from the melt and lump of Pb precipitate at the bottom of the crucible at 1373 K [Fig. 10(d)].

4. Conclusions

This paper investigates details of lead separation processes from CRT lead glass by reduction melting tests using model CRT glass containing lead oxide. Observations

Fig. 10. Schematic diagram of the reaction in the crucible and precipitation of the generated Pb. (a) room temperature to 923 K, (b) 1273 K, (c) 1361 (melting point of Na_2SiO_3)–1373 K, and (d) 1373 K.

were made with X-ray CT images of samples heated to temperatures from 673 to 1373 K containing a mixture of the model glass, Na_2CO_3 , and activated carbon. The results found that the Pb generated by the reduction settled and separated from the glass at high temperatures (above 1273 K). Further, the samples were analyzed by cross-sectional observations, XRD, XRF, and mass change determinations. It was found that Pb generation started between 923 and 973 K and that Pb settlement started at temperatures above 1273 K when the sample was fully melted. Settling and separation of the Pb were promoted by growth of Pb particles which caused by agitation of the melt with the collision and coalescence of the particles.

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